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INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
David Alan	RUSSO	AUDUBON, PENNSYLVANIA
Jeffrey Lee	STRICKER	WYNNEWOOD, PENNSYLVANIA
Ryan Christopher	SMITH	COLLEGEVILLE, PENNSYLVANIA
Thomas Dudley	CULP	DREXEL HILL, PENNSYLVANIA

 Additional inventors are being named on the 1 separately numbered sheets attached hereto**TITLE OF THE INVENTION (280 characters max)**TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF
MAKING SAME

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<input checked="" type="checkbox"/> Firm or Individual Name	Thomas F. Roland, Esq.				
Address	ATOFINA Chemicals, Inc.				
Address	2000 Market Street, 26th Floor				
City	Philadelphia	State	PA	ZIP	19103
Country	USA	Telephone	215-419-7314	Fax	215-419-7075

ENCLOSED APPLICATION PARTS (check all that apply)

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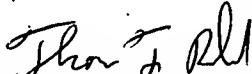
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Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME Thomas F. Roland, Esq.

TELEPHONE 215-419-7314

Date 01-23-04

REGISTRATION NO. 42,110
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Applicant(s): RUSSO, D. et al

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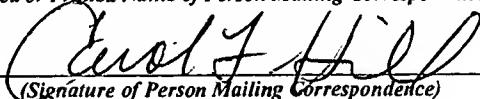
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Not yet assignedGroup Art Unit
Not yet assignedInvention: **TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME**

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INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle if any)	Family or Surname	Residence (City and either State or Foreign Country)
Roman Yurevich Gary Stephen	KOROTKOV SILVERMAN	KING OF PRUSSIA, PENNSYLVANIA CHADDS FORD, PENNSYLVANIA

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APPLICATION FOR
UNITED STATES LETTERS PATENT

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of

15

David Alan RUSSO
Jeffrey Lee STRICKER
Ryan Christopher SMITH
Thomas Dudley CULP
Roman Yurevich KOROTKOV
and
Gary Stephen SILVERMAN

20

for

25 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

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10 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

15 BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to transparent conductive oxide (TCO) films or coatings, and in particular to new multi- cation, thin film, n-type TCO films in which optimal electron 20 concentration and mobility is achieved by selecting dopants having ionic sizes that approximate those of the oxide host material, and therefore are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity.

25 The invention also relates to a method of forming TCO films or coatings by atmospheric pressure chemical vapor deposition (APCVD) of soluble solutions with a controlled crystallite size, quality and orientation to yield new n- type TCOs with enhanced electron concentration and mobility, and minimal defects.

30 The improved TCO films of the invention may be used in a variety of applications where performance of the films is affected by electron concentration and/or electron mobility, including solar control films in applications requiring a low plasma wavelength, and ohmic contact films in applications where low-resistivity is critical, such as in wide band gap semiconductor devices.

35

One of the applications of the TCO films or coatings of the invention is for use as solar control coatings, such as might be used on window glass. In general, it is desirable for such coatings to maximize transmittance of visible light while reflecting most infrared and near infrared (NIR) light. The amount of NIR light reflected depends on the
5 "plasma wavelength," which in a TCO coating or film is inversely proportional to the electron concentration in the coating. On the other hand, the transmittance of visible light by a TCO coating depends on electron mobility. In order to achieve an effective solar control coating, it is necessary to have a low plasma wavelength (or high plasma frequency), and high electron mobility. However, current thin film coating technologies
10 permit only one of the two desired properties, electron concentration and electron mobility, to be optimized in a given film.

Much of the present research on thin film TCOs has focused on increasing conductivities, particularly with respect to Indium and/or Cadmium cation combinations. See, e.g., A.J.
15 Freeman et al., MRS Bulletin, August 2000, pp. 45-51. However, even though In-Cd-O phases have some of the highest room temperature electrical conductivities measured for thin films (3500 S/cm), with mobilities as high as 200 cm²/Vs, electron concentrations were only 1×10^{20} e/cm³, well below the typical 10^{21} for doped In₂O₃ films. On the other hand, some highly conductive In-Ga-Sn-O phases have conductivities as high as 3280
20 S/cm with measured electron concentrations of 8.6×10^{20} e/cm³, but mobilities of only 24 cm²/Vs. Thus, in these prior art materials, either the electron concentration is too low to achieve an optimal plasma wavelength, or the electron mobility is too low to achieve optimal transmittance.
25 Most of the prior films were prepared using low pressure and plasma assisted chemical vapor deposition (CVD), and/or dc or rf sputtering techniques, as opposed to APCVD, as discussed above. Examples of currently used TCOs deposited by sputtering on glass include ZnO:Al, Cd₂SnO₄, Zn₂SnO₄, ZnSnO₃, ZrO₂, CeO₂, WO₃, and RuO₂. Examples of currently used TCOs may be deposited by conventional low pressure CVD include
30 ZnO:In(Al, F, Ga), SnO₂:F, TiN, and In₂O₃:Sn (ITO). The best commercial thin film

TCO coating material, $\text{In}_2\text{O}_3:\text{Sn}$, has a plasma wavelength of 1 mm with an electron concentration of 10^{21} cm^{-3} .

One of the few approaches to increasing the conductivity of TCO films by using APCVD, as opposed to conventional low pressure CVD or sputtering, is described in U.S. Patent No. 6,524,647 (Varanasi et al.), which discloses APCVD of niobium doped tin oxide films. According to the Varanesi et al. patent, niobium is especially suited for replacing tin in the tin oxide lattice because it has a similar outer shell electron configuration and a comparable atomic number to that of tin. However, Varanesi et al. fails to optimize electrical properties because it fails to recognize that a key factor is actually the ionic size of the dopant, rather than atomic number or outer shell electron configuration.

In contrast, the present invention seeks to enable the ideal balance between electron concentrations, by selection of dopants according to the ionic size of the dopant relative to the oxide matrix, and appropriate control of the APCVD process used to deposit the doped oxides. None of the above-mentioned processes takes into account ionic size for the purpose of optimizing electron concentration and/or electron mobility.

20 SUMMARY OF THE INVENTION

It is accordingly a first objective of the invention to overcome the disadvantages of the prior art by providing TCO films having improved electrical properties, and that can be produced in an efficient and cost-effective manner.

25 It is a second objective of the invention to provide TCOs having high visible transmission and improved NIR reflective properties.

It is a third objective of the invention to provide transparent conductive oxides having 30 high conductivity and an optimal combination of electron concentration and electron mobility for a given application.

It is a fourth objective of the invention to provide a method of making transparent conductive oxides that permits optimization of electron concentration and electron mobility, in order to improve visible transmission and NIR reflective properties, and/or to
5 provide films having low resistivity and high work function.

It is a fifth objective of the invention to provide a method of using APCVD to deposit TCO films or coatings having improved electrical or optical properties.

10 These objectives of the invention are accomplished, in accordance with the principles of a preferred embodiment of the invention, by a variety of new n-type TCO films in which the dopants have ionic sizes that approximate those of the metal oxide host material, and that therefore are essentially non-disruptive to the host crystal lattice, reducing electron scattering and increasing film conductivity.

15 These objectives are further achieved by using atmospheric pressure chemical vapor deposition to deposit soluble solutions having ionic sizes that approximate those of the metal oxide host material to be deposited. The resulting doped metal oxide films have higher conductivities, which in turn imparts better NIR reflective properties to the films
20 than, for example, the current state of the art tin doped indium oxide.

According to a first preferred embodiment of the invention, a metal oxide host, is deposited on a substrate in conventional fashion, but the dopants are chosen to approximately match the ionic size of the host crystals. Suitable hosts, with ionic size
25 given in parentheses, include $Zn^{2+}(0.74\text{\AA})O$, $Sn^{4+}(0.71\text{\AA})O_2$, $Ge^{4+}(0.53\text{\AA})O_2$, $Zr^{4+}(0.80\text{\AA})O_2$, $Ti^{4+}(0.68\text{\AA})O_2$, or $Ga^{3+}(0.62\text{\AA})_2O_3$, while suitable dopants according to the invention include ions such as $Sn^{4+}(0.71)$, $Bi^{5+}(0.74\text{\AA})$, $Ta^{5+}(0.73\text{\AA})$, $Hf^{4+}(0.80\text{\AA})$,
30 $Mo^{6+}(0.62\text{\AA})$, $Te^{6+}(0.59\text{\AA})$, $Nb^{5+}(0.70\text{\AA})$ and the like, all of which have sizes that approximate those of the metal oxide host material. The enhanced conductivity is manifest by both an increase of electron concentration and mobility as measured by the Hall effect.

According to a second preferred embodiment of the invention, a rutile MO₂ layer is deposited on SnO₂ or other metal oxide capable of stabilizing the rutile MO₂ film and optimize near infrared (NIR) reflection in glass/SnO₂/MO₂ bilayers and 5 glass/SnO₂/MO₂/SnO₂ sandwich structures. Suitable rutile MO₂ materials include but are not limited to M = Ti, V, Cr, Mo, Ru, or mixed alloys thereof.

According to a third preferred embodiment of the invention, Sn_xM_{1-x}O₂ films are deposited on a substrate, where the metal- semiconductor transition of MO₂ films is 10 modified by alloying with SnO₂, thus optimizing the NIR reflection.

According to a fourth preferred embodiment of the invention, films such as but not limited to WO₃, Mo_xO_y, A_xWO₃, and A_xMo_{1-x}O_y are deposited on a substrate where A is H, Li, Na, and K, and x = 0-2 and high enough to modify the plasma wavelength to 15 optimize the NIR reflectance. The film properties may be enhanced by APCVD deposition of WO₃ or Mo_xO_y on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into WO₃.

20 Electron concentrations ranging from 7-10x10²⁰e/cm³ are possible with the novel n-type TCO films deposited by the above-described processes, as well as electron mobilities of 50-150 cm²/vsec. In addition, these doped metal oxide films can be undercoated with one or more functional layers that can act as barrier layers to ion migration from the glass, anti-iridescent layers to reduce reflected color, and/or nucleation layers to alter the 25 orientation of the TCO layer(s).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a table illustrating the properties of MO₂ compounds with rutile structure 30 manufactured according to the principles of the first preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be apparent from the examples set forth below, this invention provides a variety

5 of new n-type TCO films, each having an ideal balance between electron concentration and mobility, by selecting dopants that are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity. According to the method of the invention, the films are deposited on heated substrates such as glass by APCVD of organometallic precursors combined with specific dopants and other
10 additives such that the deposited films have a higher electron concentration. The higher electron concentration is due to the incorporation of dopant ions in the host oxide lattice that cause little or no disruption of the lattice parameters, thereby decreasing electron scattering and increasing conductivity.

15 In a first preferred embodiment of the invention, doped metal oxide films are prepared by APCVD on a suitable substrate, such as soda lime glass, the metal oxides having crystal lattice host sizes ranging from .60Å to .80Å. Therefore, according to the principles of the invention, the ionic sizes of the dopants are also chosen to be approximately within this range. For example, suitable metal oxide hosts include, but are not limited to,

20 $Zn^{2+}(0.74\text{\AA})O$, $Sn^{4+}(0.71\text{\AA})O_2$, $Ge^{4+}(0.53\text{\AA})O_2$, $Zr^{4+}(0.80\text{\AA})O_2$, $Ti^{4+}(0.68\text{\AA})O_2$, and $Ga^{3+}(0.62\text{\AA})_2O_3$, the ionic sizes of which are set forth in the parentheses. Ideal dopants for these metal oxide hosts include ions such as $Sn^{4+}(0.71)$, $Bi^{5+}(0.74\text{\AA})$, $Ta^{5+}(0.73\text{\AA})$, $Hf^{4+}(0.80\text{\AA})$, $Mo^{6+}(0.62\text{\AA})$, $Te^{6+}(0.56\text{\AA})$, $Nb^{5+}(0.70\text{\AA})$ and the like, as well as combinations of any of the above-dopants.

25

In a second preferred embodiment of the invention, the principles of the invention are applied to hetero-epitaxial growth of APCVD-deposited doped and undoped rutile MO_2 structures, where M = Ti, V, Cr, Mo, Ru or mixed alloys thereof, on a SnO_2 or other metal oxide layer suitable for stabilizing the rutile MO_2 film and optimizing the near
30 infrared reflection (NIR) in glass/ SnO_2/ MO_2 bilayers and glass/ $SnO_2/ MO_2/ SnO_2$ sandwich structures. Some of the MO_2 materials, such as CrO_2 , MoO_2 , RuO_2 , have

metallic conduction with high visible absorption. Others, such as TiO₂, are semiconductors with band gaps of 3.0 eV and high visible transparency. Still others, such as VO₂, have metal to semiconductor transitions at 340K. In all cases, however, the invention permits modification of the NIR reflectance of the coatings by depositing
5 glass/SnO₂/MO₂ bilayers and glass/SnO₂/MO₂/SnO₂ sandwich structures, where other metal oxides capable of stabilizing the rutile MO₂ layer may be substituted for SnO₂. Since the host materials crystallize in a rutile structure, as illustrated in Fig. 1, it is expected that the deposited MO₂ films will crystallize in a similar fashion to produce epitaxial like layers. Also, since lattice parameters are close to that of SnO₂ for most of
10 these materials, only small stresses are expected in (001) planes.

The third preferred embodiment of the invention involves a variation of the second preferred embodiment in which APCVD is used to grow Sn_xM_{1-x}O₂ ternary alloy system layers that modify the band gap parameters of SnO₂. By tuning the fraction of the
15 transition metal, one can obtain the necessary high NIR reflection with high electron concentration.

Finally, in accordance with the principles of a fourth preferred embodiment of the invention, APCVD is used to grow oxide coatings having the form WO₃ (as well as
20 oxides such as Mo_xO_y) and A_xWO₃, (A_xMo_{1-x}O_y), where A is H, Li, Na, and K, and x = 0-2 and high enough to modify the plasma wavelength to optimize the NIR reflectance. In one embodiment, enhanced film properties are achieved by APCVD deposition of WO₃ or Mo_xO_y films on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into
25 WO₃.

Theoretical studies of A_xWO₃ indicate the possibility of a reflectance band shift towards the visible by increasing the fraction x of alkali metals in the ternary compound.
According to a preferred embodiment of the invention, the plasma wavelength of these
30 coatings is tuned to 0.7 mm by varying the content of alkali metals in the coatings on glass and other substrates. Note that the amount of A is significantly higher than that

used in Li-doped WO₃ films prepared for their electrochromic properties, where alkali doping is typically less than a few percent. In addition, one can use Na (Li, K) diffusion from glass substrates in APCVD grown MO_y films to help promote formation of A_xMO₃. In addition, implantation or vapor deposition of films with A may be used in this
5 embodiment.

A predictive example of the first preferred embodiment of the invention, in which the doped metal oxide is tantalum doped zinc oxide, follows:

10 Predictive Example

A 2.2 mm thick glass substrate (soda lime silica), two inches square, is heated on a hot block to about 650°C. The substrate may be positioned about 25 mm under the center section of a vertical concentric tube coating nozzle. A carrier gas of dry oxygen flowing
15 at a rate of 12.5 liters per minute (lpm) is then heated to about 160°C and passed through a hot wall vertical vaporizer.

A liquid coating solution containing monobutyltin trichloride (MBTC) is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol %
20 concentration in the gas composition. A second liquid coating solution of tetraethyl orthosilicate (TEOS) and triethyl phosphite (TEP) in a 1:1 mol ratio is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition.

25 The gas mixture is then allowed to impinge on the glass substrate for about 4 seconds to deposit a mixed oxide of tin and silicon about 80 nm thick with a refractive index of about 1.70. Immediately following, a second gas mixture composed of a diethylzinc tetraethylethylenediamine complex (DEED), a nitrogen carrier gas, tantalum (V) ethoxide, water vapor and air is caused to impinge on the metal oxide coated surface for
30 about 30 seconds, resulting in a tantalum doped zinc oxide film of about 300 nm. The second gas mixture may be formed by mixing separate gas streams in a manifold just

before the coating nozzle. The water vapor and air are introduced at the top of the nozzle to minimize premature reaction with the zinc and tantalum precursors. The DEED liquid is fed via a syringe pump to a second vaporizer through which a nitrogen carrier gas is flowing at 160°C at about 10 lpm. The volume flow is preferably designed to give a 0.5
5 mol % concentration in the carrier gas.

Finally, the tantalum precursor is fed via a syringe pump to a third vaporizer through which a nitrogen carrier gas is flowing at 180 °C at about 10 lpm. The volume flow is designed to give a 0.1 mol % concentration in the carrier gas. Water is fed via syringe
10 pump into a vaporizer through which an air carrier gas was flowing at about 10 lpm. The vapor concentration is about 3 mols per mol of zinc precursor.

The bilayer film stack made by the above method is predicted to have essentially no reflected color, a visible transmission greater than 70 %, an electron concentration in the
15 range of $7\text{-}10 \times 10^{20}\text{e/cm}^3$ and a mobility above $50\text{ cm}^2/\text{v-sec}$ as measured by the Hall effect.

In a similar manner, hafnium doped zirconium dioxide, molybdenum doped gallium oxide and bismuth/tantalum doped tin oxide films could be prepared. In some cases, the
20 precursors would be placed in heated bubblers and the carrier gas would pass through a molten liquid. These examples are only illustrative of the current invention and one skilled in the art will realize that minor variations outside these embodiments do not depart from the spirit and scope of this invention.

25 Having thus described various preferred embodiments of the invention in sufficient detail to enable those skilled in the art to make and use the invention, it will nevertheless be appreciated that numerous variations and modifications of the illustrated embodiment may be made without departing from the spirit of the invention. For example, other dopant and host combinations not mentioned herein could be used. Binary and tertiary
30 dopant combinations could be found which might yield films with even higher conductivities. Other undercoat films could be used which have better barrier, anti-

reflection or nucleating layer properties than the combinations described herein. Anti-reflection layers could be placed on top of the doped metal oxide layer. Dopants could be incorporated into the host oxide layer in a gradient fashion; one dopant gradually decreasing while the other gradually increases in a continuum or step fashion. Separate 5 dopant layers could be combined. The dopants described herein all are intended to replace some of the metal host ions. The enhanced effect might also be accomplished by combining dopants of this invention with dopants such as fluorine that substitute for some of the oxygen atoms in the host matrix.

10 As a result, it is intended that the invention not be limited by the above description, but that it be defined solely in accordance with the appended claims.

What is claimed is:

1. A transparent conductive oxide (TCO) film comprising a doped metal oxide,
5 wherein the ionic size of at least one dopant in the doped metal oxide
approximates the size of the host ions in an oxide lattice in the doped metal oxide.

10 2. The TCO film as claimed in claim 1, wherein the ionic size of said dopant is
between approximately 0.6Å and 0.8Å.

15 3. The TCO film as claimed in claim 2, wherein said metal oxide is selected from
the group consisting of Zn²⁺O, Sn⁴⁺O₂, Ge⁴⁺O₂, Zr⁴⁺O₂, Ti⁴⁺O₂, Ga³⁺O₃, and
mixtures thereof, and wherein said at least one dopant is selected from the group
consisting of Sn⁴⁺, Bi⁵⁺, Ta⁵⁺, Hf⁴⁺, Mo⁶⁺, Te⁶⁺, Nb⁵⁺, and mixtures thereof.

20 4. A coated substrate comprising a substrate having directly coated thereon the TCO
of claim 1.

25 5. A transparent conductive oxide (TCO) film comprising a rutile metal oxide MO₂,
wherein M is selected from the group consisting of Ti, V, Cr, Mo, Ru, and
mixtures thereof.

6. The TCO film as claimed in claim 5, further comprising at least one M¹O₂ film
layer, wherein said M¹O₂ film layer comprises SnO₂ or other metal oxide capable
25 of stabilizing the rutile MO₂ film.

7. The TCO film as claimed in claim 6, comprising a sandwich structure of
M¹O₂/MO₂/M¹O₂.

30 8. The TCO film as claimed in claim 5, wherein said metal oxide is Sn_xM_{1-x}O₂,
where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.

9. A coated substrate comprising a substrate having directly coated thereon the TCO of claim 5.

5 10. A transparent conductive oxide (TCO) film comprising a metal oxide A_xMO_y , wherein A is selected from the group consisting of H, Li, Na, and K, x = 0-2, and M is either W or Mo.

10 11. A coated substrate comprising a soda lime glass substrate and the TCO film as claimed in claim 10, wherein the metal oxide is deposited on the soda lime glass substrate with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase with incorporation/implantation of A into A_xMO_y .

15 12. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor including at least one dopant having an ionic size that approximates a size of host ions in an oxide lattice in the metal oxide.

20 13. The method as claimed in claim 12, wherein the ionic size of said dopant is between approximately 0.60Å and 0.80Å.

25 14. The method as claimed in claim 12, wherein said metal oxide is selected from the group consisting of $Zn^{2+}O$, $Sn^{4+}O_2$, $Ge^{4+}O_2$, $Zr^{4+}O_2$, $Ti^{4+}O_2$, $Ga^{3+}O_3$, and mixtures thereof, and wherein said at least one dopant is selected from the group consisting of Sn^{4+} , Bi^{5+} , Ta^{5+} , Hf^{4+} , Mo^{6+} , Te^{6+} , Nb^{5+} and mixtures thereof.

30 15. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide wherein said metal oxide is rutile MO_2 , and M is selected from the group consisting of Ti, V, Cr, Mo, Ru and mixtures thereof.

16. The method of claim 15 wherein multiple metal oxide films are deposited by APCVD, wherein said multiple films comprise M^1O_2/MO_2 bilayers or $M^1O_2/MO_2/M^1O_2$ sandwich structures, wherein said M^1O_2 film layer comprises SnO₂ or other metal oxide capable of stabilizing the rutile MO₂ film.

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17. The method of claim 15 wherein said metal oxide is Sn_xM_{1-x}O₂, where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.

10 18. A method of depositing metal oxide films by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide, wherein said metal oxide is A_xMO_y wherein A is selected from the group consisting of H, Li, Na, and K, x = 0-2, and M is either W or Mo.

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Fig. 1. MO_2 compound properties with rutile structure

MO_2	a, Å	c, Å	$V \sim 10^{-23} \text{ cm}^3$	$N_{\text{site}}(\text{Sn}) \sim 10^{22}, \text{ cm}^{-3}$	$N_{\text{site}}(\text{O}) \sim 10^{22}, \text{ cm}^{-3}$	% dopant (O)*	$E_G, \text{ eV}$	Thermal Expansion	Plasma \sim_p, \sim_m
SnO_2	4.738	3.187	7.115	2.8	5.6	3.57	3.8	0.02	1.3 ($7 \sim 10^{20} \text{ cm}^{-3}$)
TiO_2	4.585	2.95	6.2	3.22	6.45	3.1	3.0	0.114	
MnO_2	4.396	2.871	5.548	3.6	7.2	2.7	Metal	0.05	

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* - the required incorporation of a singly charged donor F, Cl, Br on O lattice site to obtain $n = 2 \sim 10^{21} \text{ cm}^{-3}$ with the plasma wavelength of 0.77 nm .

ABSTRACT OF THE DISCLOSURE

A variety of new n-type TCO films including films with dopants having ionic sizes that approximate those of the metal oxide host material, films with stabilized rutile 5 MO_2 , and films with A_xMO_y . The films are deposited by APCVD.